

ART. XXIII.—*The Essential Oil from the leaves of Agonis flexuosa.*

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Agonis flexuosa, D.C. (N.O. Myrtaceae) is a tree of low but very foliaceous appearance abounding in South-Western Australia, where it is known as "Willow Myrtle," or sometimes as "Peppermint."

Being somewhat ornamental, it is frequently grown in streets with species of eucalypts.

The narrow, coriaceous leaves are covered with numerous oil-glands, and when crushed emit an odour similar to that from many species of eucalypts.

Baron von Mueller in describing this tree in his "Select Extra-Tropical Plants," mentions that it yields an oil of "high antiseptic value," but no record has been found of any systematic examination of this oil, and the present paper aims at doing for this important oil-yielding tree what has already been done for most of our eucalypts.

By courtesy of Mr. J. Cronin, the director, supplies of the leaves were obtained from the Melbourne Botanic Gardens. Although the trees there are not in their natural habitat, the conditions of growth were not considered sufficiently abnormal to have any appreciable effect on the oil; in fact, it is probable that, as in the eucalypts, species is the main factor determining the character of the oil, and that climate, soil, etc., have but little effect. The age of the tree and the season of collection do, however, appear to have some slight influence on the yield and composition of the oil.

For this reason supplies of leaves were obtained at different seasons of the year; the first in March, 1913—early autumn—and the second in July, 1913—mid-winter. The former was distilled the day after cutting, and the second after a delay of about a week. This delay has been shown, by experiments carried out in connection with a similar investigation, to be of much less consequence than might be supposed.

Altogether about 17 ounces of the oil were obtained from the distillation of slightly over one hundredweight of leaves, and the yield, physical properties and composition of the two samples showed only insignificant differences. [Vide Table I.]

The Crude Oil.

The crude oil is of a greenish colour, closely resembling in appearance that of *E. globulus*, but its odour is quite distinctive, suggesting cineol, cymene and a phenol as some of the constituents. It is soluble in less than its own volume of 80 per cent. alcohol, but requires four volumes of 70 per cent. alcohol.

In addition to the two above-mentioned samples of oil, a third, distilled some 32 years ago, and which was possibly the sample described by Baron von Mueller, was obtained from the Botanic Gardens Museum.

TABLE I.

Physical Properties of Oils from Agonis flexuosa.

Oil.	Date of Collection.	Yield.	α_{15}°	μ_{15}°	δ_{15}°	Cineol.
I.	- March, 1913	- 1.0% _c	- + 5.3°	- 1.4657	- .900	- 72.2% _c
I(a).	- March, 1913	- —	- + 5.3°	- 1.4654	- .905	- 72.5% _c
II.	- July, 1913	- 0.8% _c	- + 4.6°	- 1.4701	- .908	- 62.0% _c
III.	- About 1881	- —	- + 3.8°	- 1.4686	- .917	- 79.1% _c

Oil I(a). is a portion of oil I., from which the phenol has been removed. The cineol has been estimated by absorption in a saturated aqueous solution of resorcin—a method that has proved more satisfactory in our experience than the older phosphoric acid method.

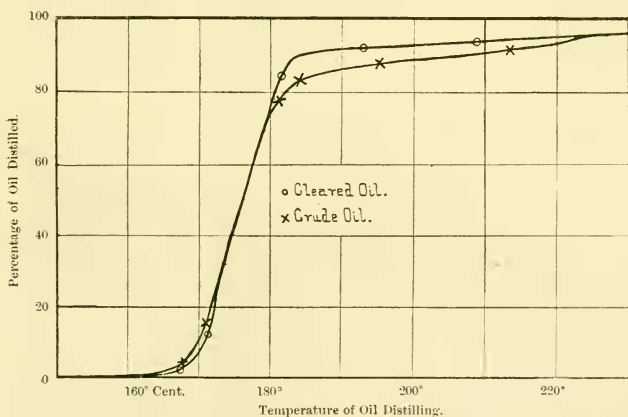
Cleared Oil.

The first sample of oil obtained—the autumn collection—was then investigated.

Phenols.—It was first treated to remove phenols. To do this 125 c.c. of the oil were shaken with a normal aqueous solution of sodium hydroxide until the phenols were dissolved; the aqueous solution was then separated, shaken out with ether to remove adhering oil, and then acidified. The separated phenols were extracted with ether and evaporated to a constant weight. The phenol was a dark yellowish-brown liquid, with a smell, strongly suggesting creosote. It was almost insoluble in water, but dissolved easily in 80 per cent.

alcohol. The addition of aqueous ferric chloride solution to this alcoholic solution produced a red coloration. Also a drop of strong nitric acid, added to a weak aqueous solution, caused a magenta coloration. There was, however, insufficient phenol to allow of any further examination.

Aldehydes.—The next step in the examination was the isolation and identification of aldehydes. The oil, after the removal of the phenol, was well washed with water and then treated with a saturated aqueous solution of sodium bisulphite, with repeated shakings for several hours. No crystalline compound was formed, and the aqueous portion on investigation showed no traces of any aldehydic compound having been formed. Similar examinations of the fractions boiling below 170 deg. C. and above 190 deg. C. respectively also gave negative results, so there can be no doubt that aldehydes, so often occurring in and depreciating the value of eucalyptus oils, are absent from this oil.



Fractional Distillation.

To isolate, as far as possible, the remaining constituents of the oil, fractional distillation was resorted to. The cleared oil was fractionated to identify the substances present in the oil. The crude oil was also fractionated and the physical properties of the fractions examined [vide Table II.]. The accompanying graph shows the distillation curves for both crude and cleared oils.

TABLE II.
Physical Properties of Fractions.

Fraction	Temperature	Volume of Fraction	α_{15}	μ_{15}°	δ_{15}°	Cineol Content of Fraction.
I.	- below 170°	- 5.5 c.c.	- —	- 1.4641	- .893	- 2.7 c.c.
II.	- 170° - 174°	- 12.0 c.c.	- $+8^{\circ}.1$	- 1.4649	- .897	- 7.7 c.c.
III.	- 174° - 178°	- 13.0 c.c.	- $+3^{\circ}.0$	- 1.4650	- .906	- 9.1 c.c.
IV.	- 178° - 187°	- 12.0 c.c.	- $+0^{\circ}.8$	- 1.4658	- .911	- 8.6 c.c.
V.	- 187° - 227°	- 5.5 c.c.	- —	- 1.4738	- .916	- 6.1 c.c.
VI.	- above 227°	- 2.0 c.c.	- —	- —	- —	- 0.8 c.c.
Whole Oil		- 50.0 c.c.	- $+5^{\circ}.3$	- 1.4657	- .900	- 35.0 c.c.

A table of this kind is extremely useful in pointing out possible constituents. For instance, fraction IV. is practically optically inactive, and yet on determining its cineol content we have accounted for only two-thirds of the fraction. This suggests the presence of another optically inactive substance of about the same boiling point as cineol, and further investigation confirms this.

Identification of Chief Constituents.

Cineol.—As stated earlier, the camphoraceous odour of cineol is noticeable in the crude oil. To confirm its presence, syrupy phosphoric acid was poured on to the oil in a test tube—equal quantities of each—and the mixture shaken up and held under a running tap for a minute, when it solidified, proving the presence of cineol. This test also proved the absence of aromadendrene, as the solid was white, for, if it were present, a brownish-red coloration would have been produced. For the quantitative estimation of cineol, the resorcin method was used. The results obtained were:—In whole oil, 72.2 per cent. In fractions, 70 per cent. A phosphoric acid estimation was also carried out, giving slightly lower results, but not sufficiently different to cast any doubt on the more consistent resorcin results.

Pinene.—Fractions I., II. and III. of the cleared oil was separately decineolised by resorcin. The residues from fractions I. and II. had distinct pinene odours, and were therefore tested for pinene thus: 2 c.c. of the oil were cooled; 7 c.c. of Amyl nitrite were added and then 4 c.c. of glacial acetic acid. The mixture was then cooled with ice and kept cooled while equal parts of glacial acetic acid and concentrated hydrochloric acid were added, drop by drop, with stirring, as long as the liquid was blue in colour. Crystals gradu-

ally separated out until there was a fairly heavy precipitate of pinene nitrosochloride, proving the presence of pinene in the oil.

Cymene.—The residue of fraction III., above mentioned, consisting of 3.5 c.c., had a lemon-like odour, strongly suggestive of cymene. It was oxidised by heating on a water-bath with 6 gms. of potassium permanganate and 180 gms. of water, until the reaction was complete, shown by the absence of oil on the surface of the aqueous solution. The oxide formed was filtered off and evaporated to dryness. The potassium salt was then boiled out with alcohol and evaporated, the residue being dissolved in water and acidified. The separated acid was re-crystallised from alcohol and melted at 155 deg. C., thus showing that it was p-oxyisopropyl-benzoic acid, and thereby proving the prior presence of cymene in the oil.

No Phellandrene.—Phellandrene is absent, a fact proved by the following test:—2 cc. of the oil were taken, and 3 c.c. of saturated aqueous solution of potassium nitrite were added, without mixing. Then ten drops of glacial acetic acid were slowly added, and the test tube, containing this, put aside to stand. No crystals formed, therefore there is no phellandrene in the oil.

Esters.—The saponification number found by the usual method is 7.5, which is equivalent to 2.6 per cent. of an ester, having the composition $C_{10}H_{18}O$.

Alcohol.—Acetylation by the ordinary method gave 7.6 per cent. of an alcohol, having the composition $C_{10}H_{18}O$.

No Free Acid.—There is no free acid in the oil, which is shown by shaking a known weight of the oil with a measured quantity of alcoholic sodium hydroxide solution for a minute and then titrating back with a standard acid.

SUMMARY.

The main constituents of the oil are, therefore, cineol, cymene and pinene. It also contains small amounts of alcohol, phenol and ester, but no phellandrene, aromadendrene, aldehyde or free acid.

It has a very pleasant odour, and owing to its high content of cineol, should prove commercially valuable. The abundance of trees in certain districts, and their foliaceous habits of growth allow of an extremely economical collection of leaves. The percentage yield, though not high, is sufficiently large to make a payable proposition, and so, taking all these factors into consideration, there is scope for the development of a new industry in South-Western Australia.

The supply of leaves in Melbourne unfortunately being restricted, this investigation was not so complete as the author should have wished; but if this paper causes an increased interest in a well-known but little investigated tree and its products, he will feel amply repaid.

Finally, he has to thank Professor Masson and Dr. Heber Green, of the Chemistry Department, University of Melbourne, for the kindly interest taken and generous assistance given in the prosecution of this research.

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